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(8) For the promising antitumor properties of indecine *N*-oxide (N.S.C. No. 132319), see V. K. Rao and T. J. McBride (Pfizer Inc), U.S. Patent 3 717 710; *Chem. Abstr.*, **78,** 140, 417b (1973).

(9) A. J. Aasen, C. C. J. Culvenor, and L. W. Smith, *J. Org. Chem.*, **34,** 4137 (1969). The structure of hastanecine was first established by K. G. Untch and D. J. Martin, *Ann. Rept. Mellon Inst., 52nd,* 11 (1965).

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(11) The same result can be formulated by examination of the preferred conformation of the starting olefin, **11**. If it be assumed that the group CH═C(a)b is s-trans relative to the β-phthalimidoethyl function in the pre-insertion conformer, it is readily seen that the vinylic hydrogen, which becomes C_{7aH}, will be trans to the methine hydrogen which emerges at C_7 of the necine bases.

(12) The preparation of **15** by phase-transfer Gabriel reaction,[1] followed by ozonolysis, is more straightforward than direct Michael addition of potassium phthalimide to acrolein; see O. A. Moe and D. T. Warner, *J. Am. Chem. Soc.*, 71, 1251 (1949).

(13) This is undoubtedly a diastereomeric mixture owing to the additional chirality in the tetrahydropyranyloxy function. At the level of chromatographic properties or spectral analysis this diastereomerism was not manifested and the two diastereomers are treated as a single entity.

(14) The structure assigned to this compound is in accord with (a) its infrared, NMR and mass spectra and (b) its C, H, and N combustion analysis within 0.4% of theory.

(15) Small amounts, ~5%, of *E* isomer were produced from the reaction and removed by silica gel chromatography; cf. E. N. Marvell and T. Li, *Synthesis,* 457 (1973).

(16) E. J. Corey and J. W. Suggs, *Tetrahedron Lett.*, 2647 (1973).

(17) For the combination of stereospecific intramolecular carbene insertions and stereospecific inversion in the acid-catalyzed opening of an activated cyclopropane, see G. Stork and M. Marx, *J. Am. Chem. Soc.*, **1,** 2371 (1969).

(18) For a recent case where intermolecular inversion of configuration of an activated cyclopropane was used for purposes of achieving stereochemical control of a pendant center relative to a ring center, see B. M. Trost, D. F. Taber, and J. B. Alper, *Tetrahedron Lett.*, 3857 (1976).

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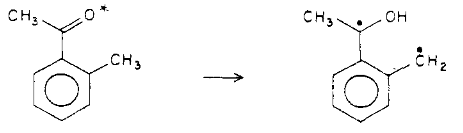
Role of Biradical Intermediates in the Photochemistry of *o*-Methylacetophenone

Sir:

The literature on the photoenolization of *o*-alkyl-substituted acetophenones and benzophenones is as abundant as it is confusing.[1] The process involves hydrogen abstraction from the γ position, i.e., as shown in eq 1.



(1)

It has been reported that reaction 1 occurs from two different excited states.[2,3] Lindqvist et al.[2] have suggested that the reaction takes place from both singlet and triplet states, while Wagner and Chen[3] have proposed that the two species involved are the syn and anti conformers of the triplet state of the ketone (**1** and **2**). The triplet state of **1** decays with a rate constant of $5 \times 10^9\ s^{-1}$. The decay of triplet **2** is controlled by bond rotation and has a rate constant of $3 \times 10^7\ s^{-1}$ in benzene.[3]

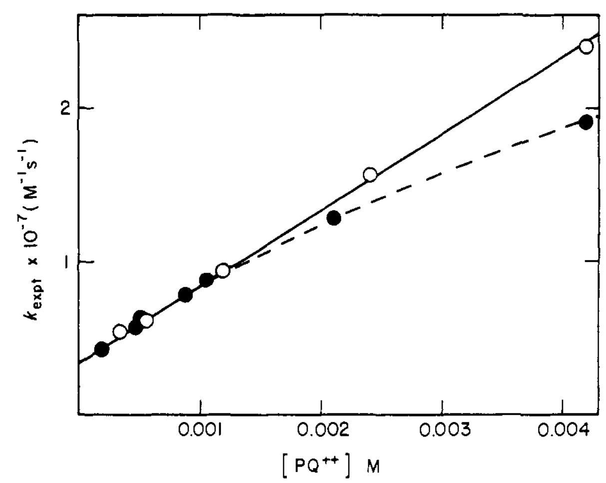
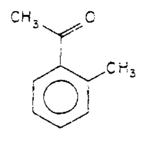
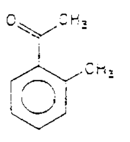


Figure 1. Plot of k_{expt} vs. $[PQ^{2+}]$ for *o*-methylacetophenone (○) in methanol containing 0.1 M *cis*-1,3-pentadiene and (●) containing no diene.



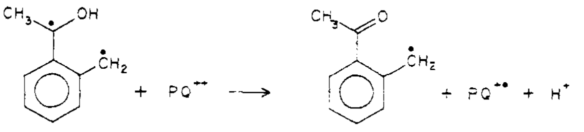
1



2

In this study we use a laser flash photolysis technique to examine the behavior of the biradical intermediate.[4] A nitrogen laser (400 kW, 337.1 nm, ~8-ns pulse duration) was used for excitation and the techniques employed are the same which we have recently developed for the study of the biradicals involved in the Norrish type II reaction.[6] We attempt to answer the following questions. (i) What is the lifetime of the biradical? (ii) Does the behavior of the biradical of reaction 1 resemble that of the biradicals produced in the Norrish type II reaction? (iii) Do we produce only one kind of biradicals as required by Wagner's mechanism,[3] or two, as apparently required[7] by Lindqvist's? (iv) What is the nature and rate constant of the interaction of oxygen with the biradicals?[5]

When biradicals having ketyl radical sites react with 1,1′-dimethyl-4,4′-bipyridilium dications (paraquat, PQ^{2+}) they produce the stable paraquat radical ion, $PQ^{+\cdot}$.[6,8] Reaction 2 illustrates the behavior in the case of the biradical form *o*-methylacetophenone.



(2)

The formation of $PQ^{+\cdot}$ follows pseudo-first-order kinetics, with a rate constant k_{expt}, which corresponds to[6b]

$$k_{expt} = \tau_B^{-1} + k_2[PQ^{2+}] \qquad (3)$$

where τ_B is the lifetime of the biradical intermediate. Figure 1 shows the results for a series of experiments in methanol. The experiments in the presence of 0.1 M *cis*-1,3-pentadiene were carried out to eliminate the reaction from the long-lived triplet state.[3] The addition of diene does not affect the intercept or the initial slope; therefore, the quenchable and nonquenchable biradical precursors produce intermediates with the same lifetime and reactivity toward PQ^{2+}. We propose that the same biradical is produced from the short- and long-lived precursors, which supports Wagner's proposal[3] that these are the syn and anti conformers of the ketone triplet. From Figure 1, we obtain $\tau_B = (300 \pm 40)$ ns[9] and $k_2 = (4.8 \pm 1.0) \times 10^9\ M^{-1}\ s^{-1}$. The curvature observed in the absence of diene probably reflects the breakdown of the assumption of very fast biradical generation at high PQ^{2+} concentrations under these conditions. In related systems[6c] we have established that this effect usually reflects the presence of a relatively long-lived triplet.[10]

In the region where the two lines in Figure 1 overlap, the yield of $PQ^{+}\cdot$ is proportional to the biradical input. From the ratio of radical-ion yields in the presence and absence of diene, we conclude that 23% of the biradicals are derived from the long-lived triplet in methanol as solvent.

The quantum yields of radical-ion formation increase with increasing PQ^{2+} concentration and $\Phi(PQ^{+}\cdot)^{-1}$ vs. $[PQ^{2+}]^{-1}$ gives a linear plot as can be expected from the mechanisms proposed.[6]

We have also examined the interaction of the biradical with oxygen, using the same techniques as described previously.[11] We found that the biradicals react with oxygen with a rate constant of $4.6 \times 10^9\ M^{-1}\ s^{-1}$; the value is in line with the reactivity of other biradicals[6,11] and typical free radicals.[12] This scavenging effect has been observed by Findlay and Tchir,[5] who attribute it to quenching of the triplet enol to produce ground-state enol; as a result, the quantum yield of the latter is increased. Further, they suggest[5] that the triplet enol is the species identified as the triplet ketone by Lindqvist et al.[2] While our results agree with those of Findlay and Tchir,[5] we believe that they can be explained by the intermediacy of biradicals in the same way as in the Norrish type II reaction, where the interaction of oxygen with the biradicals results in an enhancement of the quantum yields.[11,13] The effect is similar to that of polar solvents.[14] The lack of oxygen effect on the quantum yields[5] in polar solvents probably reflects the stabilization of the biradicals by alcohols which leaves little room for oxygen enhancement of the yields. In the case of *o*-alkyl-substituted benzophenones the effect of oxygen is not yet clear.[15]

In conclusion, the transient produced by intramolecular hydrogen abstraction in *o*-methylacetophenone has a lifetime of 300 ns, which most likely is determined by the rate of spin inversion;[6c] it reacts in the electron transfer to paraquat dications in the same manner as the biradicals produced in the Norrish type II reaction (e.g., from γ-methylvalerophenone).[6] The same biradical is apparently produced from both triplet states as required by Wagner's mechanism,[3] the long-lived triplet accounting for 23% of the biradicals produced in methanol. The biradical interacts with oxygen at nearly diffusion controlled rates.

Finally, a comment on the experimental technique seems pertinent. The method used has the obvious disadvantage that the transient of interest is not observed directly. However, as many as five transients are sometimes detected in this type of reactions.[17] In view of the complexity inherent to such a system, it is perhaps an advantage to use a technique which might be somewhat indirect but is specific for the only good electron donor involved.

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(2) H. Lutz, E. Breheret, and L. Lindqvist, *J. Chem. Soc., Faraday Trans 1*, **69**, 2096 (1973).

(3) P. J. Wagner and C.-P. Chen, *J. Am. Chem. Soc.*, **98**, 239 (1976).

(4) Some authors have questioned the use of the term biradical for the product of reaction 1 which can also be described as the triplet state of the enol.[5] We have prefered to use the term "biradical" simply because it describes best the properties exhibited in this work.

(5) D. M. Findlay and M. F. Tchir, *J. Chem. Soc., Faraday Trans 1*, **72**, 1096 (1976).

(6) R. D. Small and J. C. Scaiano, *J. Photochem.*, **6**, 453 (1976/77); *J. Phys. Chem.*, **81**, 828 (1977); *ibid.*, in press.

(7) In Lindqvist's mechanism[2] the biradicals would be produced with different multiplicity, which would be expected to lead to different biradical lifetimes.[6b,c]

(8) The radical ions, $PQ^{+}\cdot$ were fully characterized using transient spectroscopy, as well as generating concentrations of $\sim 10^{-5}$ M and examining the spectrum in a Cary 14 spectrophotometer. Triplet acetophenone and ground-state enols do not generate the radical ion.

(9) In experiments in the absence of PQ^{2+}, we observed a transient with decays with $\tau \sim 400$ ns and which has essentially the same spectroscopic properties as the species with $\tau \sim 1200$ ns reported by Lutz and Lindqvist.[2] The decay does not strictly follow first-order kinetics, probably reflecting the underlying absorbances of precursors and products. These experiments will be discussed in detail in a full paper.

(10) The lifetime of the triplet state responsible for this effect must approach or somewhat excede 100 ns to interfere with the linearity of the plot in Figure 1.[6c]

(11) R. D. Small, Jr., and J. C. Scaiano, *Chem. Phys. Lett.*, **48**, 354 (1977).

(12) J. A. Howard in "Free Radicals", Vol. II, J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, p 3.

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(14) P. J. Wagner, *Acc. Chem. Res.*, **4**, 168 (1971).

(15) While steady-state irradiation experiments have led to the suggestion of a reaction between the biradical and oxygen,[16] laser photolysis experiments have not detected such interaction.[17]

(16) M. Pfau, E. W. Sarver, and N. D. Heindel, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **268**, 1167 (1969).

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(18) The research described herein was supported by the Division of Physical Research of the U.S. Energy Research and Development Administration. This is Document No. NDRL-1766 from the Notre Dame Radiation Laboratory.

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Electron Spin Resonance Spectrum of $[(MeO)_3B\cdot B(OMe)_3]^-$. A Novel σ Radical with a One-Electron Bond

Sir:

We wish to report the ESR detection and identification of the dimer radical anion of trimethyl borate. This radical is of more than cursory interest because it resembles the prototype species H_2^+ and the ethane positive ion $C_2H_6^+$ in having essentially a one-electron bond between two atoms or groups which are identical.[1,2] Moreover, we believe this is the first electron-deficient σ radical of this type to be characterized by ESR studies.[3] Although Kasai and McLeod[4] have reported the ESR spectrum of $B_2H_6^-$ which is isoelectronic with $C_2H_6^+$, the hyperfine parameters were found to be consistent with the retention of the bridged D_{2h} structure of the parent diborane molecule.[4,5]

Whereas previous work has shown that the BF_3^- radical anion is generated by γ irradiation of a *dilute* solid solution of BF_3 in tetramethylsilane at 77 K,[6] we now find that a paramagnetic color center (λ_{max} 550 nm) containing two equivalent boron atoms is produced by γ irradiation of *crystalline* $B(OMe)_3$ at the same temperature. Taken together with the finding that BF_3^- and the $B(OMe)_3$ dimer center are photobleachable under the same conditions, these preparative details strongly suggest that a dimer radical anion is formed as a result of the consecutive reactions

$$B(OMe)_3 + e^- \rightarrow B(OMe)_3^- \tag{1}$$

$$B(OMe)_3^- + B(OMe)_3 \rightarrow [(MeO)_3B\cdot B(OMe)_3]^- \tag{2}$$

reaction 2 being facilitated in the trimethyl borate crystal. Similarly, the dimer radical anion of acetonitrile is produced by γ irradiation of the upper crystalline phase of acetonitrile